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13. ABSTRACT: One of the great challenges facing the materials field is developing suitable methods for designing new materials with chosen properties. Assembling ones from clusters, i.e., producing nanostructured or cluster assembled materials, is a promising approach that we are exploring. The research program commenced April 1, 1994, with work devoted to an investigation of Met-Cars and related small metal-compound clusters. During the course of this study we found that binary metal Met-Cars, even comprised of metals that do not yield the pure Met-Car structure, can be formed. This gives promise of attaining the ability to tailor the design of materials of specific desired properties. In related studies, we found that Met-Cars undergo a substantially delayed ionization mechanism analogous to thermionic emission, which further points to their unique electronic properties. During the course of the program, we made valuable progress in elucidating mechanisms of formation and characterizing the bonding and structure of Met-Cars. Investigations of collision-induced dissociation revealed the unique stability of the $M_6C_{12}$ stoichiometry and provided new evidence for the nature of the bonding of the lattice cage. An investigation of Met-Car adducts also has provided further understanding of the stability and bonding of various ligation complexes, and showed an analogy between their "adsorption" to Met-Cars and to their bonding with certain metal surfaces. These findings are yielding new information about Met-Cars, as well as the nature of new complexes which can be formed from these nanophase materials. In addition to studies devoted to determining their mechanisms of formation and their physical and chemical properties in gas-phase experiments, effort has been underway to develop efficient methods of synthesizing the bulk materials.			
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## **CLUSTERS OF TRANSITION METAL COMPOUNDS:** **BUILDING BLOCKS OF NEW MATERIALS**

### **I. Introduction**

Currently there is extensive interest in systems of finite size as they often give rise to unique properties that differ from those of an extended solid or the individual molecular constituents of which they are comprised. Particularly interesting are systems whose composition can be selectively chosen, and ones whose individual characteristics will be retained, allowing them to serve as the building blocks for nanostructured/cluster-assembled materials.

In 1992 we discovered a new class of molecular clusters termed metallocarbohedrenes, or Met-Cars for short, which involve bonding between early transition metals and carbon. Calculations, as well as recent experimental findings, suggest that these species exhibit considerable free electron behavior which promises to become manifested through changing electronic energy levels with the nature of the metal, and the onset of collective giant dipole resonances in the optical absorption spectrum. Indications that it is possible to produce Met-Cars with various endohedral atoms, as well as the recent finding that other metals and non-metal atoms may also be substituted in the cage lattice, suggest that these cluster materials will be particularly valuable in the context of unraveling the properties of condensed matter of finite size. This also opens an avenue for exploring the prospect that they can provide building blocks for new materials. Unraveling the properties of Met-Cars and exploring efficient methods for their production constitutes the primary objectives of the research.

### **II. Brief Overview of Progress in our Laboratory Pertaining to Studies of Metallocarbohedrenes and Related Cluster Materials**

The research program commenced April 1, 1994, with work devoted to an investigation of metallocarbohedrenes, or Met-Cars, and related small metal-compound clusters. In addition to studies devoted to determining their mechanisms of formation and their physical and chemical properties in gas-phase experiments, effort has also been underway to develop efficient methods of synthesizing the bulk materials. During the course of the program, we have made valuable progress in elucidating mechanisms of formation and characterizing the bonding and structure of Met-Cars. Investigations of collision-induced dissociation have revealed the unique stability of the  $M_8C_{12}$  stoichiometry and provided new evidence for the nature of the bonding of the lattice cage. An investigation of Met-Car

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adducts also has provided further understanding of the stability and bonding of various ligation complexes, and has shown an analogy between their "adsorption" to Met-Cars and to their bonding with certain metal surfaces. These findings are yielding new information about Met-Cars, as well as the nature of new complexes which can be formed from these nanophase materials. In addition, during this grant we found that binary metal Met-Cars, even comprised of metals which do not yield the pure Met-Car structure, can be formed. This gives promise of attaining the ability to tailor the design of materials of specific desired properties. In other work, we found that Met-Cars undergo a substantially delayed ionization mechanism analogous to thermionic emission which further points to their unique electronic properties. Finally, we have conducted some studies of the mechanisms of cluster ionization using ultrafast laser pump-probe techniques to lay a foundation for methods to explore the dynamics of Met-Car relaxation following their excitation.

Details of many of our accomplishments have already been submitted for publication and have either appeared in print, or are in press; see the listing in Section IIIa. Other work is in progress, and publications of the findings are in preparation. During the report period we published and or submitted 16 papers for publication dealing with work supported through this grant. In addition, work sponsored by this grant was reported at numerous scientific conferences, academic colloquia and industrial seminars; these are listed in Section IIIb.

#### **A. Formation and Structure of Metallocarbohedrenes**

During the grant, experiments were performed to shed further light on the several possible structural configurations that have been suggested for the Metallocarbohedrene molecular cluster family. [See papers 388, 402, 417, 418, 433, 434, 446.] Although a  $T_h$  structure was found to be most consistent with the experimental findings, a number of the theories suggest a structure with  $T_d$  symmetry, composed of a tetracapped tetrahedral metal skeleton. The major difference between the experimentally proposed pentagonal dodecahedron of  $T_h$  symmetry and the aforementioned  $T_d$  structure lies in the number of distinct metal sites on the surface of the cluster. For the  $T_h$  structure, each metal site in the cluster occupies an identical position leading to only one type of metal environment; however, there are two distinct positions for the metal sites in the tetracapped tetrahedron structure, four each in the inner tetrahedron, and four in the outer tetrahedron. These sites are distinguishable by various preferred coordination numbers.

Recently, we have performed experiments utilizing binary metal containing Met-Cars composed of  $Ti_xZr_yC_{12}$  (where  $x+y=8$ ) to provide further experimental information regarding the type of environment at each of the metal sites in the cluster. These experiments were performed utilizing various compositions of TiC and Zr powders exposed to direct laser vaporization (DLV) without supersonic expansion to cool the cluster as occurs in the usual laser vaporization (LAVA) molecular beam type experiment. The mass spectral data acquired with mixtures of widely varying composition revealed a smooth decrease in intensities of the mass peaks which correspond to the progression  $Ti_8C_{12}$ ,  $Ti_7ZrC_{12}$ ,  $Ti_6Zr_2C_{12}$ , etc., continuing through the evenly substituted  $Ti_4Zr_4C_{12}$  cluster. See Figure 1. As one would expect, if there were only one type of metal site, a statistical substitution results. Details of the findings are given in paper 433. [It is worthy of note that most experimental data based on a variety of methods continue to be consistent with the structure of  $T_h$  symmetry.]

The study of Met-Car ligation complexes provides another approach to determine the number of distinct metal sites available. It has been suggested that previous gas phase titration experiments could not completely rule out the  $T_d$  symmetry since the titrants of water and ammonia might be too small to distinguish these two sets of metal atoms in a tetracapped tetrahedral structure. In order to resolve this argument, 2-butanol, which is much larger than water and ammonia, and should give rise to steric effects upon attachment to those two sets of metal atoms, was reacted with titanium Met-Cars. As seen in Figure 2, the product distribution of  $Ti_8C_{12}^+$  with 2-butanol showed no preference for the attachment of four molecules, and the product intensity was found to smoothly continue until truncation at  $Ti_8C_{12}^+(2\text{-butanol})_8$ . This experimental result provides further evidence that all eight metal atoms are equivalent in Met-Cars and further supports the originally proposed dodecahedral structure with  $T_h$  symmetry. See paper 417.

It has been long noticed that interactions of  $Ti_8C_{12}^+$  with polar molecules, which terminate at  $Ti_8C_{12}^+(\text{polar molecules})_8$ , are different from those with  $\pi$ -bonding molecules, which are observed to terminate at  $Ti_8C_{12}^+(\pi\text{-bonding molecules})_4$ . In order to further clarify the bonding interactions, several molecules including acetonitrile, pyridine, and acetone, which have both  $\pi$ -bond(s) and a dipole moment, were selected and reacted with  $Ti_8C_{12}^+$ . A product distribution truncation at  $Ti_8C_{12}^+(M)_4$  ( $M$  stands for the molecules mentioned above) was commonly observed along with small peaks of  $Ti_8C_{12}^+(M)_{5,6}$ . In the case of the dodecahedral structure of Met-Cars, four  $\pi$ -bonding molecules may

attach onto the pentagonal faces by bridging the two Ti atoms contained in each face. This explains the experimental findings from our laboratory; see details given in paper 417.

## B. Delayed Ionization / Thermionic Emission

Studies of Met-Cars using time-of-flight spectrometry often show mass resolution which is much lower than what is instrumentally achievable with other systems. This observation, coupled with the fact that previous results suggested that the Met-Car molecular clusters could be easily ionized with almost any laser wavelength, led us to an investigation of the ionization dynamics of this system.

In recent studies in our laboratory, ionization occurring on a time scale orders of magnitude longer than what is characteristic of normal photoionization was observed only for Met-Cars, but not for the rest of the metal-carbon cluster distribution (see papers 415, 418, 429, 435). See Figure 3. In order for delayed ionization to be observed for the Met-Car clusters, the clusters must have some way to accommodate the energy necessary for the ionization to occur, while at the same time not dissociating into smaller cluster fragments. Metallocarbohedrenes are ideal systems to exhibit this behavior, because comparison of the recently measured value for the ionization potential (IP) [1,2] and the theoretically predicted value for the dissociation energy( $E_{diss}$ ) [3] shows that a favorable relationship ( $IP/E_{diss} \leq 1$ ) exists for this family of cluster molecules. This favorable relationship and the large density of electronic states for these transition metals-carbon species, allows the cluster to "store" the energy gained during the excitation and ionize during the time scale of the experiment. These findings for the delayed ionization of metallocarbohedrenes are consistent with a process that parallels the bulk phenomena of thermionic emission. At high laser fluences, above approximately 50 mJ/cm<sup>2</sup>, a second delayed channel which corresponds to an atomic ion emission was observed. See Figure 4.

Neither of these delayed ion formation channels exhibits a dependence on the laser excitation wavelengths of 532 and 355 nm, but each channel showed a strong dependence on the fluence of the excitation laser. Similar findings have been seen consistently in all of the Met-Car systems studied, including  $Ti_8C_{12}$ ,  $V_8C_{12}$ ,  $Zr_8C_{12}$ , as well as the binary metal containing Met-Cars  $Ti_xZr_yC_{12}$  and  $Ti_xNb_yC_{12}$  (where  $x+y=8$ ). See Figure 5. Further, for the delayed atomic ion emission channel, only  $Ti^+$  has been observed for the binary metal Met-Car systems. Clearly, metallocarbohedrene molecular

clusters do possess interesting electronic properties that may be able to be controlled through the inclusion of various 'dopant' metals into the cagelike structural motif.

### C. Photodissociation

Photodissociation and photoionization studies have been shown to be of considerable value in obtaining quantitative data on the physical and chemical properties of small clusters. They can yield information on dissociation dynamics, potential energy surfaces, stabilities, structure and electronic states. Studying the properties of metallic- and semiconductor-like clusters of varying size and electronic character provides a way of ascertaining the onset of collective effects in materials as they transcend from the isolated molecule to the size domain in which behavior attributable to the condensed state becomes displayed. Molecular clusters comprised of Met-Cars are especially suitable materials for elucidating these and related optical and electrical properties of systems of finite size, since they can be produced from transition metals of varying electronic character, and substitution of other components into the cage has been shown possible. Calculations, as well as various experimental findings, suggest that these systems display considerable free electron behavior which promises to become manifested in the observation of differing electronic energy levels with the nature of the metal, quantum size effects, and the onset of collective giant dipole resonances in the optical absorption spectrum.

Due to the confined sizes of these systems, and the fact that mixed metal clusters can be formed, it is possible to vary the number of "free electrons" in cages of comparable geometry. Hence, these new materials offer the promise of new variants for studying isolated quantum wells and quantum dots, potentially useful for doping semiconductor and other electronic materials. Varying the electronic character should also enable an alteration and selection of the optical properties of these systems. Investigating these aspects comprises an important component of our work.

In order to investigate the stability of various members of the Met-Car cluster family, we recently undertook a study of the photofragmentation of Met-Car cluster ions. See paper 446. Pilgrim and Duncan [4] previously studied many of the single metal Metallocarbohedrene systems (see Table 1), as well as some larger, probably cubic metal-carbon cluster systems. The goal of our study was to determine how the photofragmentation of several members of the binary metal Met-Car cluster family

compared to previously reported results for the single metal Met-Cars, as well to determine whether or not there is a preference as to which metal in a binary metal Met-Car is lost first.

Three clusters were chosen for study to determine the effect of the overall electron count on the stability of the binary Met-Car cluster:  $Ti_7YC_{12}$ ,  $Ti_7ZrC_{12}$ , and  $Ti_7NbC_{12}$ . The  $Ti_7ZrC_{12}$  cluster is isoelectronic to the initially discovered  $Ti_8C_{12}$ , while the  $Ti_7YC_{12}$  contains one less metal electron, and the  $Ti_7NbC_{12}$  contains one more. Preliminary electronic calculations carried out in our laboratory have suggested that the substitution of a yttrium atom into the Met-Car structure destabilizes the structure, while the substitution of a niobium atom contributes to a greater stability. These same results show that there is not an appreciable change in the stability of the cluster upon a substitution of a zirconium atom for one of the titanium atoms. By comparing the resulting photofragments for each of the above clusters, any differences in the bonding sites between the different metals may be discerned. See Figure 6.

The photoionization-photodissociation time-of-flight apparatus utilized in our laboratory shown in Figure 7, incorporates a reflectron located at the terminus of the first quadrupole bender; it can be accessed by turning off the potentials to the bender (right side of figure). Briefly, the technique is implemented as follows: A pulsed, supersonic neutral cluster beam is generated by a laser vaporization source. The clusters are thermalized by a suitable buffer gas and further cooled in the subsequent supersonic expansion effected into vacuum through the conical-shape nozzle. After the supersonic jet is skimmed at the end of the main expansion chamber, it enters the ionization chamber. Photoionization is accomplished with tunable light from a WEX system pumped by a dye laser coupled to the frequency doubled, tripled, or quadrupled output of a second Nd:YAG laser. A second dye laser and WEX is available for two-color experiments. The cluster ions thus produced are then mass analyzed in the TOF mass spectrometer. This mass spectrometer contains a double acceleration region followed by a long field-free region. The clusters can be either directly investigated with a reflectron, or alternatively, the ion beam can be bent by a pair of quadrupole benders so that it can be separated from the neutral beam for the photodepletion studies. The ions are detected with a multichannel plate located at the end of the flight path, and the signal is collected in a digital storage oscilloscope. The lasers, pulsed valve driver, and the oscilloscope are all synchronized through a multichannel delay generator. The experimental control and data acquisition are accomplished with a PC.

A typical dissociation scan appears in Figure 8. In this series of spectra, each successive photofragment is identified by the mass lost from the initial parent cluster. As the fragment peaks each successively line up with the initial parent, this mass loss is determined.

As can be seen in Table 2, each of the three binary Met-Cars listed above photodissociate through the successive losses of titanium atoms. While these results do not show a dependence of the photofragment on the substituted metal, this may be merely an indication that the titanium loss is simply statistically more feasible based on the 7:1 ratio of Ti to the substituted metal. However, with each successive loss, this ratio moves closer to unity, and there is no experimental indication of a loss channel which corresponds to the loss of the substituted metal. While this last observation points to the fact that there is no photofragmentation that leads to the loss of the substituted metal for the  $Ti_7M_1C_{12}$  ( $M = Y, Zr, Nb$ ) binary metal Met-Cars, these results have yet to be extended to the more highly substituted members of these binary metallocarbohedrene families. Studies related to this issue are in progress.

#### D. Collision Induced Dissociation

In order to provide further evidence for the physical stability and structure of Met-Cars compared to proximate species with differing carbon contents, we conducted collision-induced dissociation (CID) studies of vanadium- [paper 434] and titanium-carbon clusters [paper 402]. Although an analysis of the absolute dissociation energies for large, tightly bound systems is always problematic because of the kinetic shift involved, the purpose of the present studies is to further investigate the stability of the Met-Cars by studying their dissociation properties and comparing its relative CID threshold value with that of other metal-carbon clusters. Specific comparisons are made with one that is carbon-deficient, namely  $V_8C_{11}^+$ , and another that is a carbon-rich  $V_8C_{13}^+$  species; the latter is expected to have a completed cage structure similar to that of the Met-Car  $V_8C_{12}^+$ , while the former is expected to have a noncomplete cage-like structure.

The collision-induced dissociation studies of the metal-carbon clusters were made employing a triple quadrupole mass spectrometer system coupled with a laser vaporization source. Many of the  $Ti_xC_y^+$  clusters, including the Met-Car  $Ti_8C_{12}^+$ , are found to undergo primary dissociation through the loss of a neutral titanium atom. The dissociation threshold of  $Ti_8C_{12}^+$  is estimated to be about 9 eV, which is indicative of a very stable cage cluster. Multiple metal loss from  $Ti_8C_{12}^+$  is found to dominate

in multiple sequential dissociation, but sequential collisions induce fragmentation by both C<sub>2</sub> and C<sub>3</sub> units as well. No single carbon loss was observed for Ti<sub>8</sub>C<sub>12</sub><sup>+</sup> under sequential dissociation, which suggests that the carbon-carbon double bonds are important in both the formation and dissociation mechanisms of Ti<sub>8</sub>C<sub>12</sub><sup>+</sup>. Several larger Ti<sub>9,10</sub>C<sub>y</sub><sup>+</sup> clusters are observed to fragment to Ti<sub>8</sub>C<sub>12</sub><sup>+</sup>, possibly by loss of small metal-carbon units, which further proves that Ti<sub>8</sub>C<sub>12</sub><sup>+</sup> is unusually stable. The high estimated dissociation threshold for Ti<sub>8</sub>C<sub>12</sub><sup>+</sup>, its multiple collision fragmentation patterns, and the larger Ti<sub>9,10</sub>C<sub>y</sub><sup>+</sup> clusters directly fragmenting to Ti<sub>8</sub>C<sub>12</sub><sup>+</sup> provide additional evidence that Met-Cars are quite stable, which is consistent with their proposed cage-like structure. See Figure 9.

The results for the vanadium system reveal that the primary dissociation channel is loss of a metal atom for all but V<sub>8</sub>C<sub>12</sub><sup>+</sup>, which loses C<sub>3</sub> and V<sub>9</sub>C<sub>14</sub><sup>+</sup>, which loses both V and VC<sub>2</sub>. These findings are in general agreement with ones for the titanium system, except that under single-collision conditions V<sub>8</sub>C<sub>14</sub><sup>+</sup> loses a C<sub>3</sub> unit to become V<sub>8</sub>C<sub>11</sub><sup>+</sup>, while Ti<sub>8</sub>C<sub>14</sub><sup>+</sup> loses Ti. Importantly, we show that both the Met-Car V<sub>8</sub>C<sub>12</sub><sup>+</sup> and V<sub>8</sub>C<sub>13</sub><sup>+</sup> are significantly more resistant to dissociation than the neighboring V<sub>8</sub>C<sub>11</sub><sup>+</sup> cluster species. In addition to deducing the primary fragmentation products of several V<sub>x</sub>C<sub>y</sub><sup>+</sup> clusters, we also obtained results of studies of the multiple-collision dissociation patterns of both V<sub>8</sub>C<sub>12</sub><sup>+</sup> and V<sub>8</sub>C<sub>13</sub><sup>+</sup>, which are observed to undergo C<sub>2</sub> and C<sub>3</sub> loss after some metal loss has occurred. These findings are consistent with the building patterns observed for these clusters and our proposed structure for V<sub>8</sub>C<sub>12</sub><sup>+</sup>. Through study of the dissociation of V<sub>9</sub>C<sub>12</sub><sup>+</sup>, the ionization energy of V<sub>8</sub>C<sub>12</sub> is found to be less than that of the vanadium atom, i.e., less than 6.74 eV, in accord with theoretical predictions.

#### E. New Evidence for the High Stability of Neutral Met-Cars

Recently, Brock and Duncan reported experimental data of neutral titanium-carbon clusters studied by near-threshold photoionization mass spectrometry (1). In their experiment, ionization of the titanium Met-Car was accomplished under single-photon ionization conditions, enabling the fluence of the ionization laser to be approximately 5 to 1000 μJ cm<sup>-2</sup>. Power dependence studies which were carried out suggested that the ionization was accomplished under single photon conditions. The most puzzling result reported in their paper was that the Ti<sub>8</sub>C<sub>12</sub> clusters were generally seen as species of only minor abundance. From this, they raised the question whether *neutral* Met-Cars are really stable compared to the other neutrals of different metal-carbon stoichiometry.

Prompted by this apparently contradictory finding to our early work, we conducted a similar experimental study of neutral titanium-carbon clusters, but with careful attention to the conditions of Met-Car formation. See Figure 10. The new findings reveal that the dominant  $Ti_8C_{12}$  peak in the mass spectra depends strongly on the conditions of cluster production. More importantly, clear evidence for the high stability of the neutral  $Ti_8C_{12}$  was obtained. See details in paper 454.

The present findings reveal that the mass distribution can be substantially altered by varying the cluster source conditions under a constant photoionization condition. Most importantly, we found that copious quantities of the metallocarbohedrene clusters (Met-Cars),  $Ti_8C_{12}$ , are produced when the power of the vaporization laser for cluster formation is sufficiently high ( $\sim 15$  mJ pulse $^{-1}$ ). Under these conditions, an intense peak corresponding to  $Ti_8C_{12}$  is detected even at very low fluences of the laser employed to acquire single-photon ionization conditions. The present study provides clear evidence for the stability of the *neutral* Met-Cars, laying to rest the question raised by Brock and Duncan in their recent paper [1].

#### F. Intense Field-Matter Interactions: Multiple Ionization of Clusters and Coulomb Explosion

As a prelude to conducting studies of the dynamics of Met-Cars via excitation with high intensity ultrafast laser light pulses, test experiments were undertaken employing ammonia. Extending the statistical concept of covariance analysis, both positive and negative covariance was extended to cluster systems and shown to provide a valuable concept in exploring processes acting in concert from ones which are competitive. See paper 452.

The findings provided direct evidence of competitive parallel reactions involving singly charged clusters and Coulomb exploded particles that become formed when matter interacts with intense radiation in the ultrafast time region. Direct evidence was also found of the connectiveness of charged clusters with highly charged species ( $N^{7+}$ ,  $N^{4+}$ ,  $N^{3+}$ , and  $N^{2+}$ ) produced upon the interaction of molecular ammonia clusters with an intense femtosecond laser beam ( $\sim 10^{15}$  W/cm $^2$  at 120 fs). The value of covariance analysis as a general technique for studying dynamical processes in clusters was demonstrated through elucidating the details of various Coulomb explosion events. Positive covariance determinations served to identify concerted processes such as the concomitant explosion of protonated cluster ions of unsymmetrical size, while anti-covariance mapping was exploited to

distinguish competitive reaction channels such as the production of highly charged nitrogen atoms formed at the expense of the protonated members of the cluster ion ensemble. The present study demonstrates the great potential which covariance analysis offers in identifying the precursors and products of dynamical events in clusters, and in the present case has provided further support to the ignition model as a mechanism contributing to the initial ionization events in clusters leading to highly charged atomic species.

The connectiveness of protonated singly charged clusters of different sizes establishes that they arise from the Coulomb explosion of parent clusters of larger size. Although multiply charged clusters smaller in size than those stabilized by their cohesive energy are too unstable to be seen directly in the parent mass distribution, the correlations provided by covariance mapping set lower limits of the size of the neutral cluster species. See Figure 11.

The correlations also show good agreement with earlier studies in which kinetic energy measurements pointed to unsymmetric charge distributions giving rise to split peaks arising from the Coulomb explosion of protonated species [5]. And, except for a few cases, most high charge states show no correlations with singly charged species.

Importantly, the anti-correlation observed between CEPs and larger singly charged clusters presents a new concept of investigating a competitive ionization process. See Figure 12. Indeed, the anti-covariance map shows the operative nature of competitive channels in agreement with the model accounting for the possible dynamical channels available following cluster excitation; see paper 452.

Taken together, the findings support the model due to Wei et al [5] that attributes the production of protonated clusters which undergo Coulomb explosion versus the production of CEPs, to a cascading of charge transfer reactions which occur at times short compared to the motion of the nuclei. Finally, the positive covariance seen between the CEPs and small ammonia cluster ions, and the anti-covariance found for the CEPs with the larger clusters further supports the ignition model [6-8] as an important mechanism responsible for the initiation events of multicharge atom formation in clusters, which predicts only a weak dependence on cluster size. Our study shows the power of covariance mapping in studying fragmentation processes in both neutral and ionized molecular clusters.

## G. Met-Car Production

One of our goals is to produce bulk quantities of isolated materials for structural and property characterization. Assigning the exact structure of these clusters will involve the use of a variety of techniques including solid-state and liquid NMR ( $^{13}\text{C}$ ,  $^{51}\text{V}$ ,  $^{93}\text{Nb}$ ,  $^{47,49}\text{Ti}$  and  $^{91}\text{Zr}$ ), ESR, Raman, UV-Visible, and X-ray diffraction; before such analyses are made, a solid sample containing significant quantities of Met-Cars must be produced and isolated.

We have already produced small quantities of Met-Cars in the solid state using two different techniques. See papers 388 and 407. The first method employing an arc-discharge apparatus has been shown to yield small quantities of Met-Cars, but recently we have developed an improved technique. In the second method, a crucible filled with a metal carbide sample is placed in a small chamber. The chamber is first evacuated and then filled with an inert gas. Laser vaporization of the samples (e.g. TiC, ZrC, NbC, or VC) is then achieved by striking the sample with the second harmonic (532 nm) output of a Nd:YAG laser operated at approximately 11 mJ/pulse. The laser is focused on the sample through a rotating cylindrical lens generating a focal line approximately 0.5 cm long. The vaporized material collects on the surfaces of the chamber and is collected for analysis at a later time.

Laser desorption (LD) time-of-flight mass spectrometry (TOF-MS) analyses of some of the coatings produced via the second method have established that the Met-Car species are present. In these experiments the laser power is kept near threshold and the beam is loosely focused. There is a marked difference between the mass spectra of desorbed species and directly laser vaporized species. The findings show that Met-Cars are not being produced with one laser pulse and desorbed with subsequent laser pulses. Met-Car signal is observed immediately upon irradiation, and over time the signal intensity thereafter decreases. A comparison of the desorbed signal to that of  $\text{Zr}_8\text{C}_{12}$  produced in the molecular beam and via laser vaporization of metal carbide [9] shown in Table 3, shows a significant difference in the ratios of Zr and  $\text{Zr}_4\text{C}_x$  to the Met-Car peak. The reason that other  $\text{Zr}_x\text{C}_y$  species are even observed in the LD spectrum is that they correspond to the likely building blocks for the Met-Car and are therefore also present in the sample. If Met-Cars were being made using the desorption laser we would expect to see a pattern similar to that seen in Reference 9. Instead a Met-Car peak is observed which is much more prominent in the desorbed spectra. These arguments indicate that the Met-Cars can indeed be analyzed by LD TOF-MS.

Samples produced via this laser vaporization method have been subjected to extraction using a variety of solvents in a Soxhlet apparatus. Solutions produced via this extraction method have been analyzed by UV-Visible absorption spectroscopy. Preliminary results show a broad feature at approximately 704nm. Although this feature does decrease in intensity over several days, fresh extractions always show this absorption. Experiments are in progress to identify the most appropriate solvents in order to obtain good yields of isolated Met-Cars.

Recently we designed and constructed an instrument that combines both the laser vaporization (LV) production method and the Laser Desorption (LD) TOF-MS analytical technique (see Figure 13). This new instrument provides more control of the parameters during the laser vaporization event.

It is critical that we are able to vary the conditions and/or the material of the surface onto which the soot from the LV method is deposited. Our new apparatus allows us to selectively choose the material of the substrate, the ambient pressure (from a few thousand torr down to  $1 \times 10^{-6}$  torr), and the atmosphere in which the vaporization takes place. Also, it is possible to employ trapping matrices on the collection surface which could serve to encage the Met-Car and facilitate its solvation. Another reason to investigate the advantage gained by collecting in a matrix is that during the Met-Car deposition, the produced clusters might diffuse together and possibly recombine and/or decompose back into metal carbide. The matrix would serve to isolate and immobilize the Met-Cars as they impinge upon the surface, and therefore they would remain intact on the substrate. The studies of the ligated gas-phase Met-Cars can lead us to species that would be suitable as matrices for trapping Met-Cars immediately following the LV event. After LV has been performed on a sample, the new apparatus enables the coated substrate to be directly translated into the LD TOF-MS portion of the instrument for analysis, eliminating possible effects of exposure to the atmosphere. After analysis, the substrate can be translated back into the first stage of the apparatus which can be removed, isolated and moved into an argon atmosphere dry-box. At this point the sample can be prepared for extraction or other analytical techniques. The spectrometer portion of the instrument will also have the ability to analyze via laser desorption samples that have been produced by other methods.

## References

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4. J. S. Pilgrim and M. A. Duncan, *J. Am. Chem. Soc.* **115**, 6958 (1993).
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6. E. M. Snyder, S. A. Buzzia, and A. W. Castleman, Jr., *Phys. Rev. Lett.* **77**, 3347 (1996).
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### IIIa. List of Publications Sponsored by AFOSR Since This Grant Commenced April 1, 1994

388. "Met-Cars: A New Class of Cluster Materials," A. W. Castleman, Jr., in *Recent Advances in the Physics and Chemistry of Fullerenes*, (K. M. Kadish and R. Ruoff, Eds.) Electrochemical Society, NJ, pp 346-359 (1994).
402. "Collision Induced Dissociation of Titanium-Carbon Cluster Cations," K. P. Kerns, B. C. Guo, H. T. Deng, and A. W. Castleman, Jr., *J. Chem. Phys.* **101**, 8529-8534 (1994) .
407. "Met-Cars: A New Family of Metal-Carbon Clusters," A. W. Castleman, Jr., in *Applications of Organometallic Chemistry in the Preparation and Processing of Advanced Materials* (J. F. Harrod and R. M. Laine, Eds.) NATO ASI Series E: Appl. Sci., Vol. 297, Kluwer Academic Publishers, The Netherlands, pp 269-281 (1995).
415. "Delayed Ionization and Delayed Atomic Ion Emission of Ti and V Metallocarbohedrenes: Evidence for Collective Electronic Effects," B. D. May, S. F. Cartier and A. W. Castleman, Jr., *Chem. Phys. Lett.* **242**, 265-272 (1995).
417. "Studies of Met-Car Adducts:  $Ti_8C_{12}^+(M)_n$  (M=halogens,  $\pi$ -bonding molecules and polar molecules), H. T. Deng, K. P. Kerns, and A. W. Castleman, Jr., *J. Am. Chem. Soc.* **118**, 446-450 (1996).
418. "Dynamics of Cluster Reactions and Ionization: From Semiconductor to Hydrogen-Bonded/van der Waals Systems," A. W. Castleman, Jr., B. D. May, S. F. Cartier, K. P. Kerns, H. T. Deng, E. M. Snyder, and S. A. Buzzia, *NATO ASI Series on Large Clusters of Atoms and Molecules*, Kluwer Academic, Dordrecht, pp 371-404 (1996).

429. "The Delayed Ionization and Atomic Ion Emission of Binary Metal Metallocarbohedrenes  $Ti_xM_yC_{12}$  ( $M = Zr, Nb; 0 \leq y \leq 4; x + y = 8$ )," S. F. Cartier, B. D. May and A. W. Castleman, Jr., *J. Chem. Phys.* **104**, 3423-3432 (1996).

433. "On the Formation, Structure and Stabilities of Metallocarbohedrenes," S. F. Cartier, B. D. May and A. W. Castleman, Jr., *J. Phys. Chem.* **100**, 8175-8179 (1996).

434. "Collision Induced Dissociation of Vanadium-Carbon Cluster Cations," K. P. Kerns, B. C. Guo, H. T. Deng and A. W. Castleman, Jr., *J. Phys. Chem.* **100**, 16817-16821 (1996).

435. "Delayed Ionization of and Delayed Atomic Emission from Metallocarbohedrenes," B. D. May, S. F. Cartier, and A. W. Castleman, Jr., in *Science and Technology of Atomically Engineered Materials* (P. Jena, S. N. Khanna, B. K. Rao, Eds.) World Scientific, Singapore, pp 207-214 (1996).

438. "Clusters: Structure, Energetics, and Dynamics of Intermediate States of Matter," A. W. Castleman, Jr. and K. H. Bowen, Jr., Centennial Issue of *J. Phys. Chem.* **100**, 12911-12944 (1996).

440. "The Influence of Solvation on Ion-Molecule Reactions," A. W. Castleman, Jr., in *Advances in Gas Phase Ion Chemistry* (L. M. Babcock and N. G. Adams, Eds.) JAI Press, Connecticut, in press.

444. "Clusters in Intense Laser Fields: Multiple Ionization and Coulomb Explosion," E. M. Snyder, D. A. Card, D. E. Folmer and A. W. Castleman, Jr., in *Resonant Ionization Spectroscopy 1996*, (N. Winograd and J. Parks, Eds.), Institute of Physics Series, AIP Press, 379-382 (1997).

446. "Photodissociation of Binary Metal Metallocarbohedrenes," B. D. May, S. E. Kooi, B. J. Toleno and A. W. Castleman, Jr., *J. Chem. Phys.* **106**, 2231-2238 (1997).

452. "Covariance Mapping of Ammonia Clusters: Evidence of the Connectiveness of Clusters with Coulombic Explosion," D. A. Card, D. E. Folmer, S. Sato, S. A. Buzzia, and A. W. Castleman, Jr., *J. Phys. Chem.* **101**, 3417-3423 (1997). Also note cover.

454. "Titanium-Carbon Clusters: New Evidence for High Stability of Neutral Met-Cars," H. Sakurai and A. W. Castleman, Jr., *J. Phys. Chem.*, submitted.

### IIIb. List of Seminars, Posters, Talks, During the Report Period April 1, 1994 to Present Reporting AFOSR Sponsored Research

"Clusters: Getting the Magic Out of Magic Numbers," invited colloquium, Department of Physics and Astronomy, Rutgers University, Piscataway, NJ, April 6, 1994.

"Clusters: A World of Cages," invited seminar, Department of Chemical Engineering, Rensselaer Polytechnic Institute, Troy, NY, April 13, 1994.

"Met-Cars: Transition Metal-Carbon Molecular Clusters," invited talk, 185th Society Meeting of the Electrochemical Society on *Fullerenes: Physics, Chemistry, and New Directions VI* Symposium, San Francisco, CA, May 22-24, 1994

"Metal Cluster Alloys and Oxides: Elucidating Structural and Electronic Effects in Governing the Reactivity and Catalytic Role of Matter in Finite Dimensions," invited talk, Ninth DOE/BES Heterogeneous Catalysis Surface Chemistry Meeting, Oconomowoc, WI, May 24-27, 1994.

"Clusters and the Solid State," invited talk, 8th International Congress of Quantum Chemistry, Prague, Czechoslovakia, June 19-23, 1994.

"Metallocarbohedrenes (Met-Cars) and Their Role in Reactions and Catalysis," invited talk, Quantum Chemical Aspects of Heterogeneous Catalysis, Berlin, Germany, June 26-28, 1994.

"The Production and Properties of Met-Cars," invited talk, Eighth CIMTEC World Ceramics Congress, Florence, Italy, June 29-July 4, 1994.

"Cluster Interests Related to Catalysis and New Electronic Materials," invited talk, University Research Initiatives on Clusters and Clusters Assemblies, Annapolis, MD, July 15, 1994.

"Met-Cars: A Unique Class of Transition Metal-Carbon Molecular Clusters," invited talk, 1994 Gordon Research Conference on Inorganic Chemistry, Wolfeboro, NH, July 31-August 5, 1994.

"The Production of Individual and Binary Metal Metallocarbohedrenes by the Direct Laser Vaporization of Carbides or Metal/Carbide Mixtures," (presented by S. F. Cartier and B. D. May) American Chemical Society Meeting, Washington, DC, August 21-25, 1994.

"Binary Element Metallocarbohedrenes," (presented by H. T. Deng) American Chemical Society Meeting, Washington, DC, August 21-25, 1994.

"Met-Cars: A New Family of Metal-Carbon Clusters," invited talk, NATO ARW on Applications of Organometallic Chemistry in the Preparation and Processing of Advanced Materials," Cap d'Agde, France, September 5-9, 1994.

"Met-Cars and TiO Clusters," invited talk, DuPont Research and Development Experimental Station, Wilmington, DE, September 20, 1994.

"Met-Cars: A Unique Class of Molecular Clusters," invited seminar, Department of Chemistry, University of California, San Diego, La Jolla, CA, October 11, 1994.

"Met-Cars: A New Class of Molecular Clusters," invited colloquium, Department of Chemistry, University of Nebraska, Lincoln, NB, October 14, 1994.

"Met-Cars: A Unique Class of Molecular Clusters," invited talk, Harvard/MIT Combined Physical Chemistry Series, Harvard/Massachusetts Institute of Technology, Cambridge, MA, October 21, 1994.

"Metallocarbohedrenes: Study of a New Class of Materials and Some Other Related Transition Metal Nitrides and Silicides," 1994 Molecular Dynamics and Inorganic Materials Contractors' Conference, National Academy of Sciences, Washington, DC, October 23-26, 1994.

"Met-Cars: A Unique Class of Materials," invited seminar, Department of Chemical Engineering, Pennsylvania State University, December 1, 1994.

"Exciting Matter of Nanoscale Dimensions, 1. Clusters: A World of Cages, Magic Numbers, and Building Blocks of Condensed Matter; 2. Met-Cars: A Unique Class of Molecular Cluster Materials; 3. An Ultrafast Glimpse of Reactions in Clusters," invited Distinguished Lecture Series, *Frontiers in Chemical Research*, Texas A&M University, College Station, TX, December 5-7, 1994.

"Clusters: The Fifth State of Matter," invited seminar, Department of Chemistry, Cleveland State University, January 13, 1995.

"An Ultrafast Look at Cluster Reactions," invited seminar, Stanford University, Stanford, CA, April 10, 1995..

"Shedding Light on Met-Cars -- A Unique Class of Molecular Clusters," invited seminar, University of California, Berkeley, CA, April 11-12, 1995.

"Dynamics of Cluster Ionization Following Multiphoton Absorption of High Intensity Ultrafast Laser Pulses, invited talk, Yamada Conference XLIII on Structures of Clusters, Shimoda, Shizuoka, Japan, May 10-13, 1995.

"Clusters: The Interplay Between Experiment and Theory," invited seminar, The University of Tokyo, Japan, May 15, 1995.

"Met-Cars: A Unique Class of Molecular Clusters," invited seminar, The University of Tokyo, Japan, May 15, 1995.

"Dynamics of Cluster Ionization Following Multiphoton Absorption of High Intensity Ultrafast Laser Pulses," invited talk, The XVI International Symposium on Molecular Beams, Ma'ale Hachamisha, Israel, May 21-26, 1995.

"Shedding Light on Met-Cars: A New Class of Molecular Clusters," invited seminar, Göteborg University, Göteborg, Sweden, May 29, 1995.

"Metal Carbon Clusters," invited talk, NATO Advanced Study Institute, Erice, Italy, June 20, 1995.

"van der Waals and Hydrogen Bonded Cluster Reactions," invited talk, NATO Advanced Study Institute, Erice, Italy, June 29, 1995

"Intracluster Excited State and Ion-Molecule Reaction Dynamics of Weakly Bound Clusters," invited talk, Femtochemistry: The Lausanne Conference, Lausanne, Switzerland, September 4-8, 1995.

"Coulomb Explosion of Multicharged Clusters Produced in Intense Radiation Fields," invited talk, Optical Society of America Annual Meeting/ILS-XI Conference, Portland, Oregon, September 10-15, 1995.

"The Properties and Reactions of Binary-Metal Met-Cars," invited talk, International Symposium on the Science and Technology of Atomically Engineered Materials, Richmond, VA, October 30-November 4, 1995.

"Delayed Ionization of and Delayed Atomic Ion Emission from Metallocarbohedrenes," (poster presented by Brent D. May), International Symposium on the Science and Technology of Atomically Engineered Materials, Richmond, VA, October 30-November 4, 1995.

"Delayed Ionization and Delayed Atomic Emission from Met-Cars," poster, 1995 International Chemical Congress of Pacific Basin Societies, Honolulu, HI, December 17-22, 1995.

"The Ionization and Reaction Dynamics of Met-Cars," invited talk, 1996 Sanibel Conference on "Metal-Containing Ions and Their Applications in Mass Spectrometry," Tampa, FL, January 20-23, 1996.

"Shedding a Little Light on Clusters," invited Chemical Physics Seminar, California Institute of Technology, Pasadena, CA, February 20, 1996.

"Delayed Ionization of and Delayed Atomic Emission from Metallocarbohedrenes," poster, 1996 March Meeting of the American Physical Society, St. Louis, MO, March 18-22, 1996.

"Novel Mass Spectrometric Probes of Cluster Dynamics," invited talk, American Chemical Society Meeting, New Orleans, LA, March 25-29, 1996.

"Delayed Ionization of and Delayed Atomic Emission from Metallocarbohedrenes," invited talk, 70th Colloid and Surface Science Symposium, Clarkson University, June 16-19, 1996.

"Met-Cars: Optical Excitation and Dynamics of Ionization," invited talk, 1996 Molecular Dynamics Contractors Meeting, University of Colorado at Boulder, June 2-5, 1996.

"Coulomb Explosion of Multicharged Clusters Produced in Intense Radiation Fields," keynote talk, Eighth International Symposium on Resonance Ionization Spectroscopy and Its Application, The Pennsylvania State University, June 30-July 5, 1996.

"Metallocarbohedrene Ionization Dynamics: A Molecular Example of Thermionic Emission," (poster presented by Steven E. Kooi and Brian J. Toleno), Eighth International Symposium on Resonance Ionization Spectroscopy and Its Application, The Pennsylvania State University, June 30-July 5, 1996.

"Clusters In Intense Laser Fields: Multiple Ionization and Coulomb Explosion," (poster presented by E. M. Snyder), Eighth International Symposium on Resonance Ionization Spectroscopy and Its Application, The Pennsylvania State University, June 30-July 5, 1996.

"Delayed Ionization of and Delayed Atomic Emission from Metallocarbohedrenes," poster, Eighth International Symposium on Small Particles and Inorganic Clusters, Copenhagen, Denmark, July 1-6, 1996.

"Dynamics of Intra-Cluster Reactions via Ultrafast Time-Resolved Spectroscopy," Opening Plenary Lecture, 14th International Symposium on Gas Kinetics, Leeds, United Kingdom, September 7-12, 1996.

"Studies of Transition Metal Oxide Clusters: Gaining Insight into the Mechanisms of Catalysis," invited talk, DuPont Central Research & Development, Wilmington, DE, September 25, 1996.

"Delayed Ionization of and Delayed Atomic Emission from Metallocarbohedrenes," invited talk, Fifth Annual Workshop of the Consortium for Nanostructured Materials, Nashville, TN, October 18-19, 1996.

"Cluster Dynamics: From the Ultraslow to the Ultrafast," invited colloquium, Temple University, Philadelphia, PA, October 24, 1996.

"Cluster Dynamics: From the Ultraslow to the Ultrafast," invited seminar, Max-Planck-Institut für Quantenoptik, Garching, Germany, November 1, 1996.

"Dynamics of Ion Molecule Reactions in Clusters," invited poster presentation, 1997 Winter Gordon Research Conference on Structures, Energetics and Reaction Dynamics of Gaseous Ions; Discussion Leader for the Session on *Molecular Clusters*, Ventura, CA, February 23-27, 1997.

"Met-Cars: A Unique Class of Molecular Clusters," invited colloquium, Department of Chemistry, University of California, Irvine, February 28, 1997

"Met-Car Dynamics: Formation, Ionization and Dissociation," invited talk, 1997 American Physical Society March Meeting, Kansas City, MO, March 17-21, 1997.

"Production and Analysis of Metallocarbohedrene Containing Soot," (presented by B. J. Toleno), 1997 American Physical Society March Meeting, Kansas City, MO, March 17-21, 1997.

"Metal-Carbon Clusters: New Evidence for High Stability of Neutral Metallocarbohedrenes," (presented by H. Sakurai), 1997 American Physical Society March Meeting, Kansas City, MO, March 17-21, 1997.

"Delayed Ionization in Transition Metal Carbon Clusters," (presented by S. E. Kooi), 1997 American Physical Society March Meeting, Kansas City, MO, March 17-21, 1997.

"Clusters: A Look at Intermediate States of Matter," invited The Joe L. Franklin Memorial Lecture, Rice University, Houston, TX, April 9, 1997.

"Cluster Excitation and Ionization: From the Ultraslow to the Ultrafast," invited speaker, Special Sesquicentennial Event at the City College of New York, Symposium on Molecular Aggregates: Photochemistry, Photophysics, Spectroscopy and Nonlinear Optics, New York, NY, April 11, 1997.

#### **IV. Ph.D. and M.S. Degrees Obtained by Graduate Students Supported (in part) Through this Grant Since 1994**

**Stephen Buzzia, Ph.D.,** *Ionization Dynamics of Acetone and Ammonia Clusters: Consequences of Femtosecond Ionization* (1995), Research Scientist, International Paper

**Stephen Cartier, Ph.D.,** *Metallocarbohedrenes and Binary Metal Metallocarbohedrenes: Formation Mechanisms, Structures, Stabilities and Ionization Dynamics* (1995), Assistant Professor, Colgate University

**Dennis A. Card, M.S.,** *Covariance Mapping of Ammonia Clusters: An Analysis Tool of Time-of-Flight Mass Spectrometry* (1997), West Point Military Academy

**H. T. Deng, Ph.D.,** *Met-Cars and Oxide Clusters: Formation, Structures, and Reactivities* (1996), Postdoctoral Research Associate, University of Alberta, Canada

**K. P. Kerns, Ph.D.,** *Formation, Reactivities, and Collision Induced Dissociation of Metallocarbohedrenes (Met-Cars) and Other Metal-Carbon Cluster Ion* (1996), Postdoctoral Research Associate, Argonne National Laboratory, IL

**B. D. May, Ph.D.,** *Metallocarbohedrenes: Ionization Dynamics, Stability and Structure* (1996), Instructor, Lock Haven University, PA

**Eric M. Snyder, Ph.D.,** *Ultrafast Laser Studies of Hydrogen Bonded and van der Waals Clusters: Real-Time Dynamics and Intense Field-Matter Interactions* (1997), Senior Scientist, Premier American Technical Corp., State College, PA

**Zhouzheng (Kent) Shi, Ph.D., *Cluster study via TOFMS: Dissociation, Structure, and Reaction***  
(1995), Research Scientist, KOMAG, Inc.

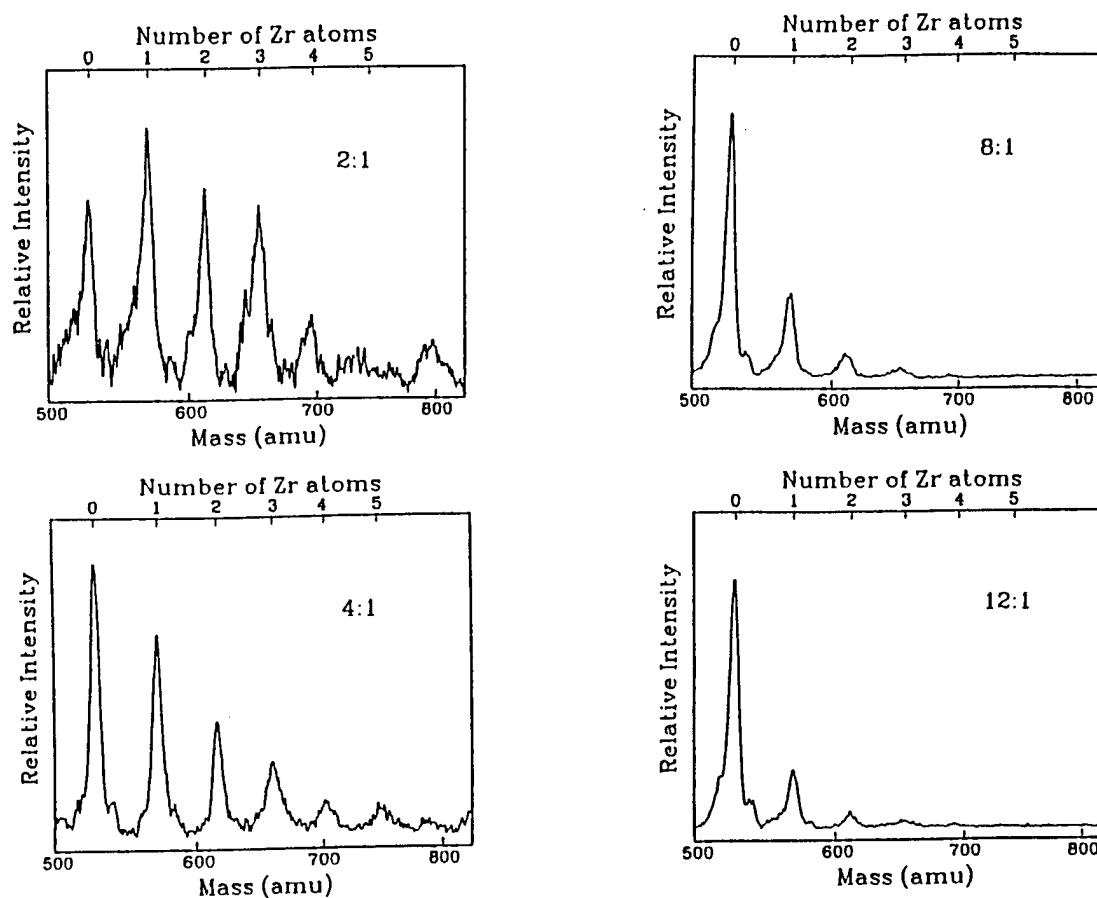
**Other Group Members Supported (in part) Through This Grant**

**Graduate Research Assistants**

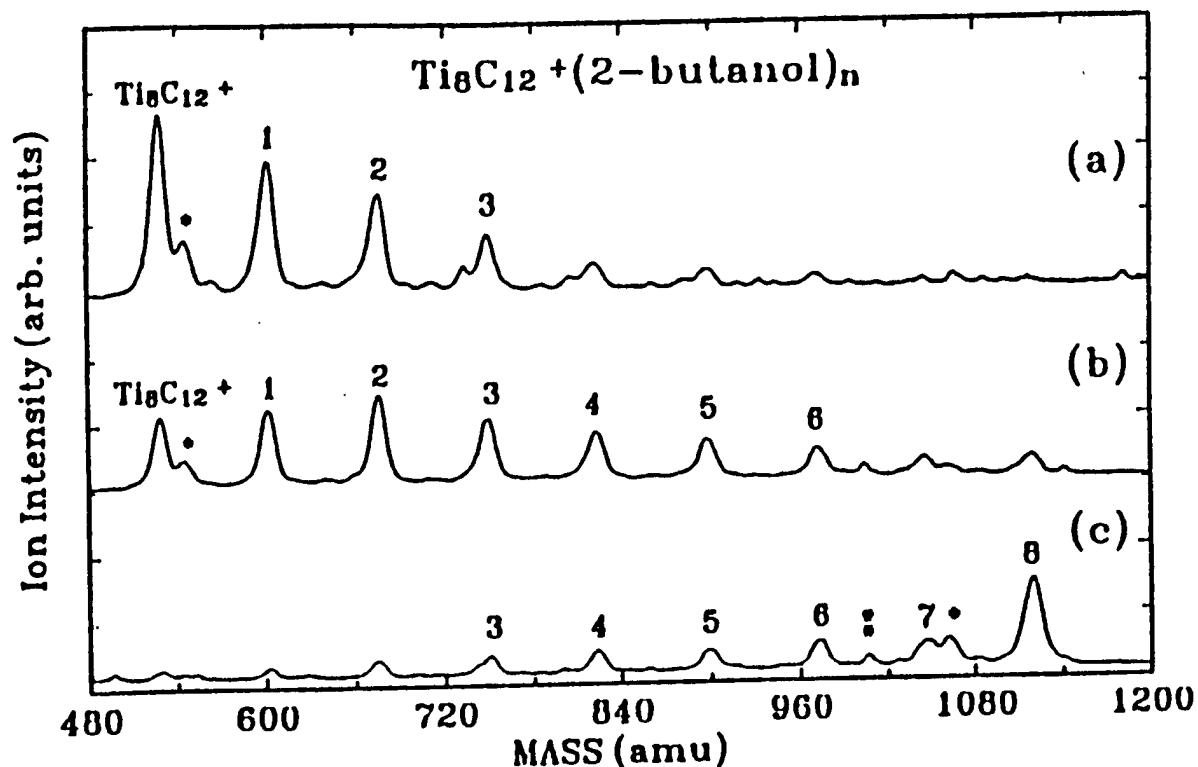
Daniel E. Folmer  
Steven E. Kooi  
Brian J. Toleno  
Hiromu Sakurai

**Postdoctoral Fellow**

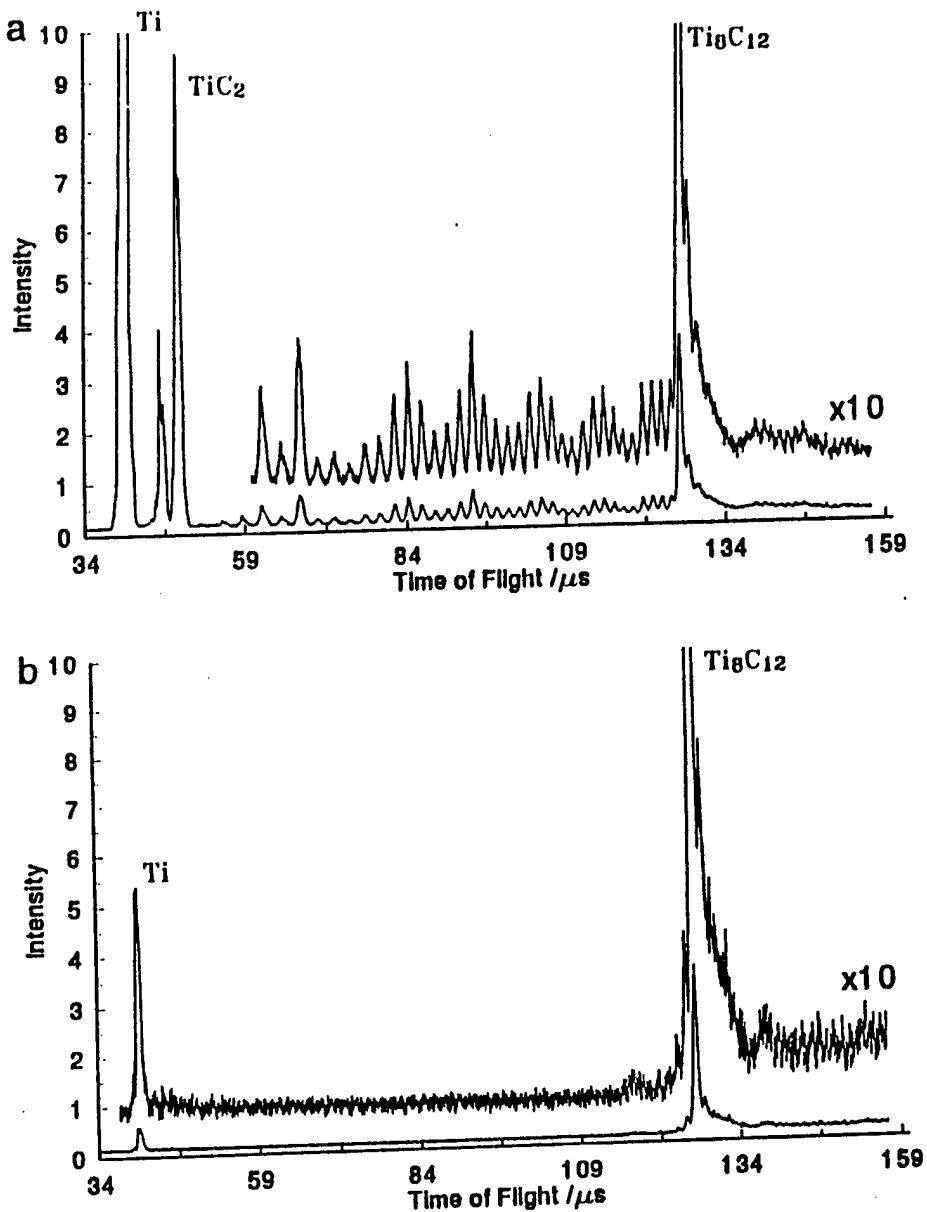
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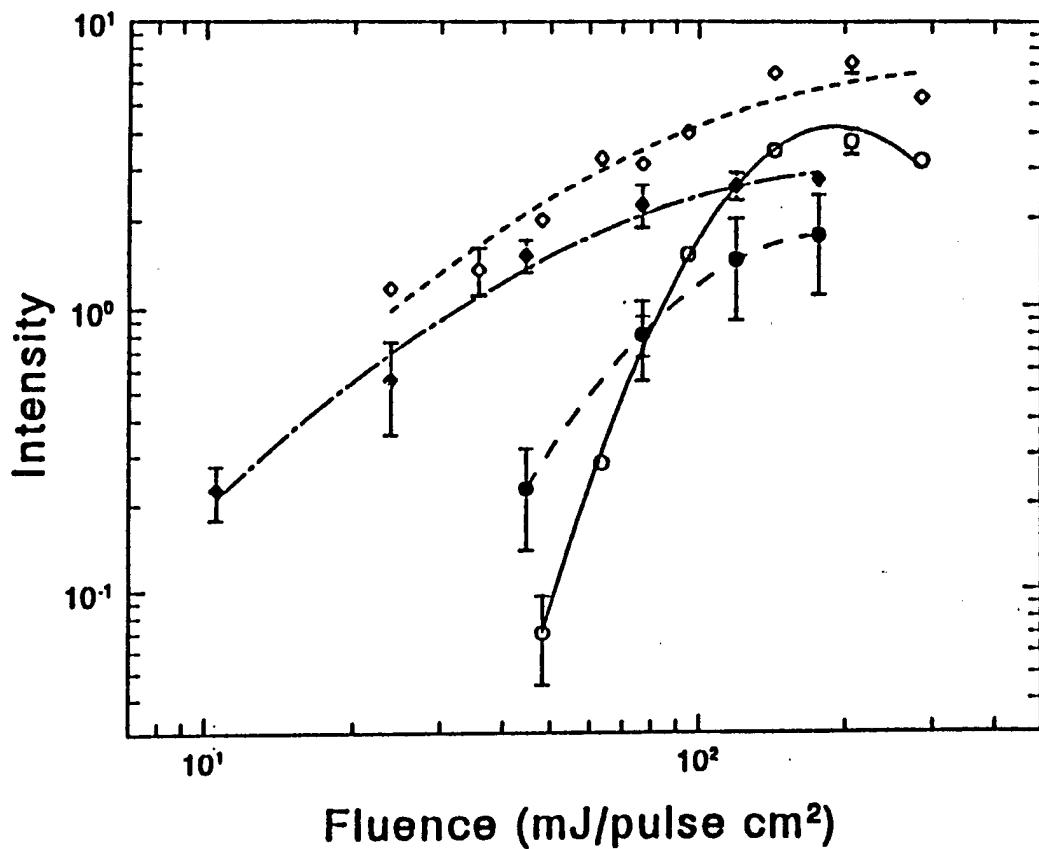
**Figure 1.** Mass spectra of  $\text{Ti}_x\text{Zr}_y\text{C}_{12}^+$  ( $x + y = 8$ ,  $0 \leq y \leq 5$ ) species obtained under direct laser vaporization conditions with the number of substituent zirconium atoms and the Ti:Zr molar ratio of the target mixture indicated.



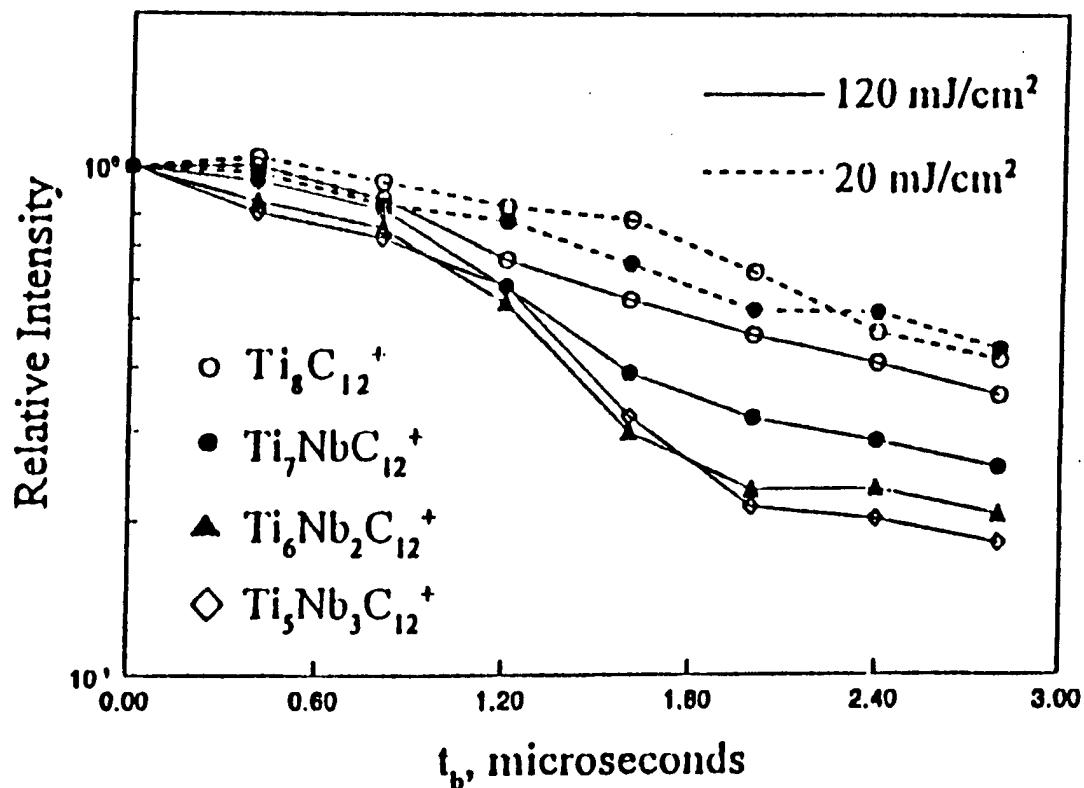
**Figure 2.** The mass spectrum of  $\text{Ti}_8\text{C}_{12}^+$  with 2-butanol at different pressures: (a) 0.65 mTorr, (b) 0.8 mTorr, (c) 1.20 mTorr. The numerals indicate the number of butanols associating onto  $\text{Ti}_8\text{C}_{12}^+$ . Note that a smooth transition in the number of 2-butanol binding onto  $\text{Ti}_8\text{C}_{12}^+$  occurs with the increase of pressure of 2-butanol; the distribution truncates at  $n = 8$ . The peaks marked by one and two asterisks are due to water and methanol impurities.



**Figure 3.** a) Mass spectrum of  $\text{Ti}_x\text{C}_y$  clusters taken at  $t_e=3\mu\text{s}$  and  $t_b=-2\mu\text{s}$ .  $\text{Ti}^+$  is shown off scale. Peaks arriving  $> 60\mu\text{s}$  after laser excitation have been magnified x20 for comparison with Figure 1b. b) Mass spectrum of  $\text{Ti}_x\text{C}_y$  clusters taken at  $t_e=3\mu\text{s}$  and  $t_b=1.5\mu\text{s}$ . Note the absence of mass peaks between  $\text{Ti}^+$  and the vicinity of  $\text{Ti}_8\text{C}_{12}^+$ , even following x20 magnification. All peaks appearing in this spectrum are delayed ions, as all peaks  $< 700$  amu due to prompt ionization are removed at this setting of the blocking field. Both spectra a and b were taken under identical laser fluence conditions of 96.5  $\text{mJ/cm}^2$ .



**Figure 4.** Laser fluence dependencies of delayed  $Ti^+$  —○— and delayed  $Ti_8C_{12}^+$  —●— 532nm and delayed  $Ti^+$  —◇— and delayed  $Ti_8C_{12}^+$  —◆— at 355nm. Error bars represent one standard deviation, and all points display error bars, some cases being represented by the size of the data point or smaller. The 355nm data represents averages of five sets of data for the  $Ti_8C_{12}^+$  and four sets of data for the  $Ti^+$ , while the 532 data represents an average of two data sets. The lines represent second order polynomial fits to the data.



**Figure 5.** Plot of signal intensities of metallocarbohedrene clusters versus  $t_b$  under two different fluence conditions.

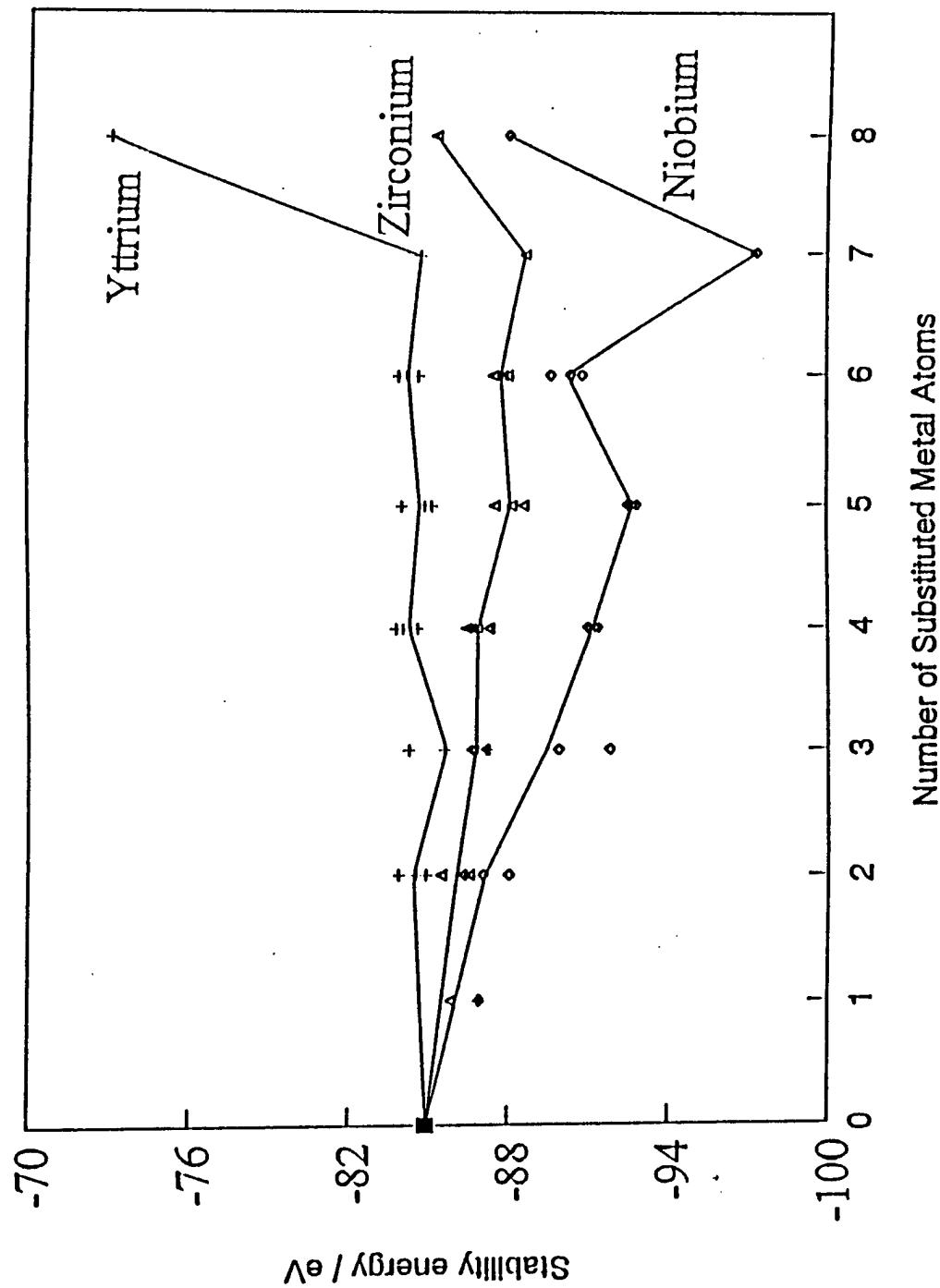


Figure 6. Plot of stability energies versus the degree of substitution. Differing M-C bond distances are accounted for.

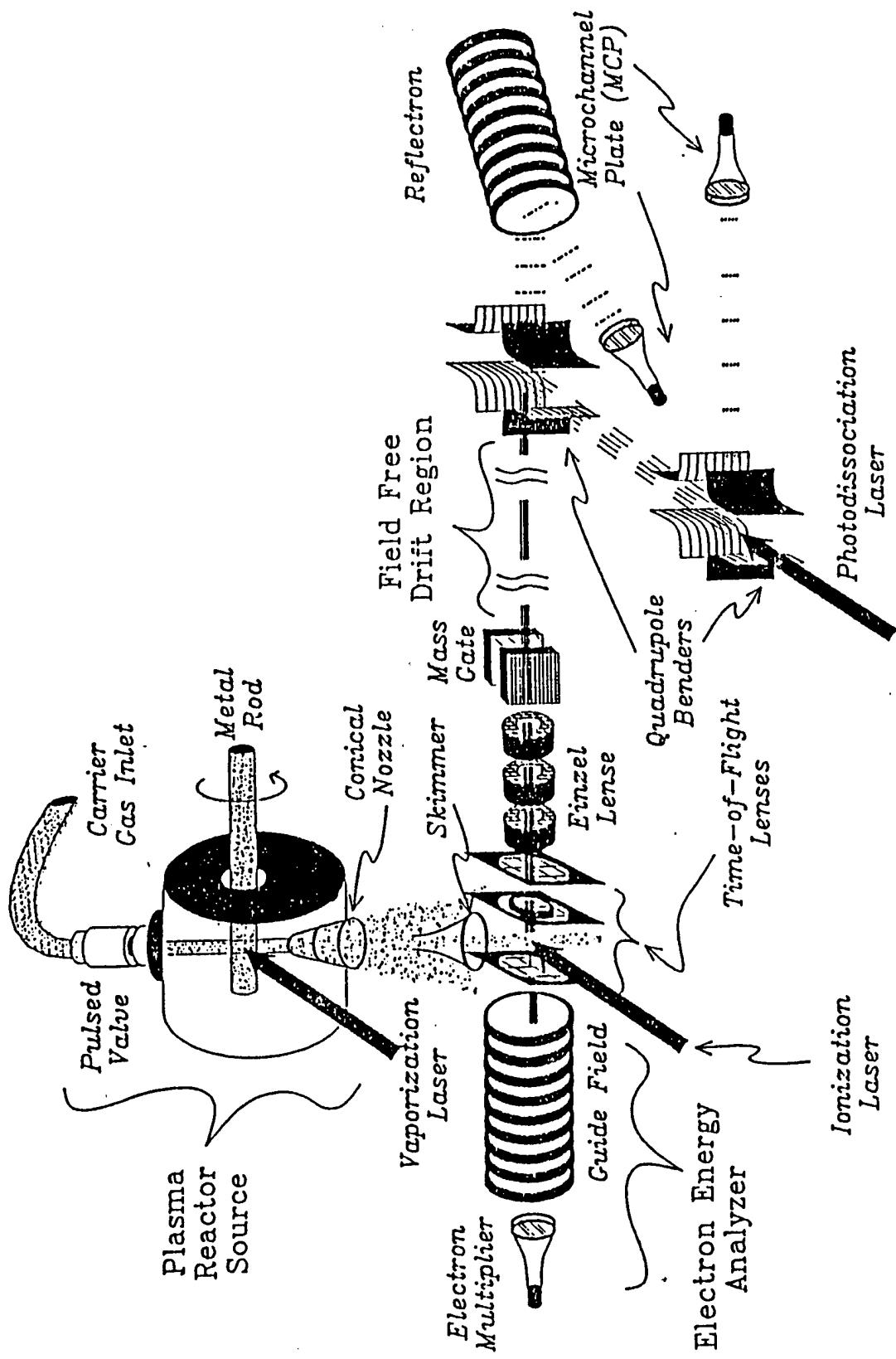
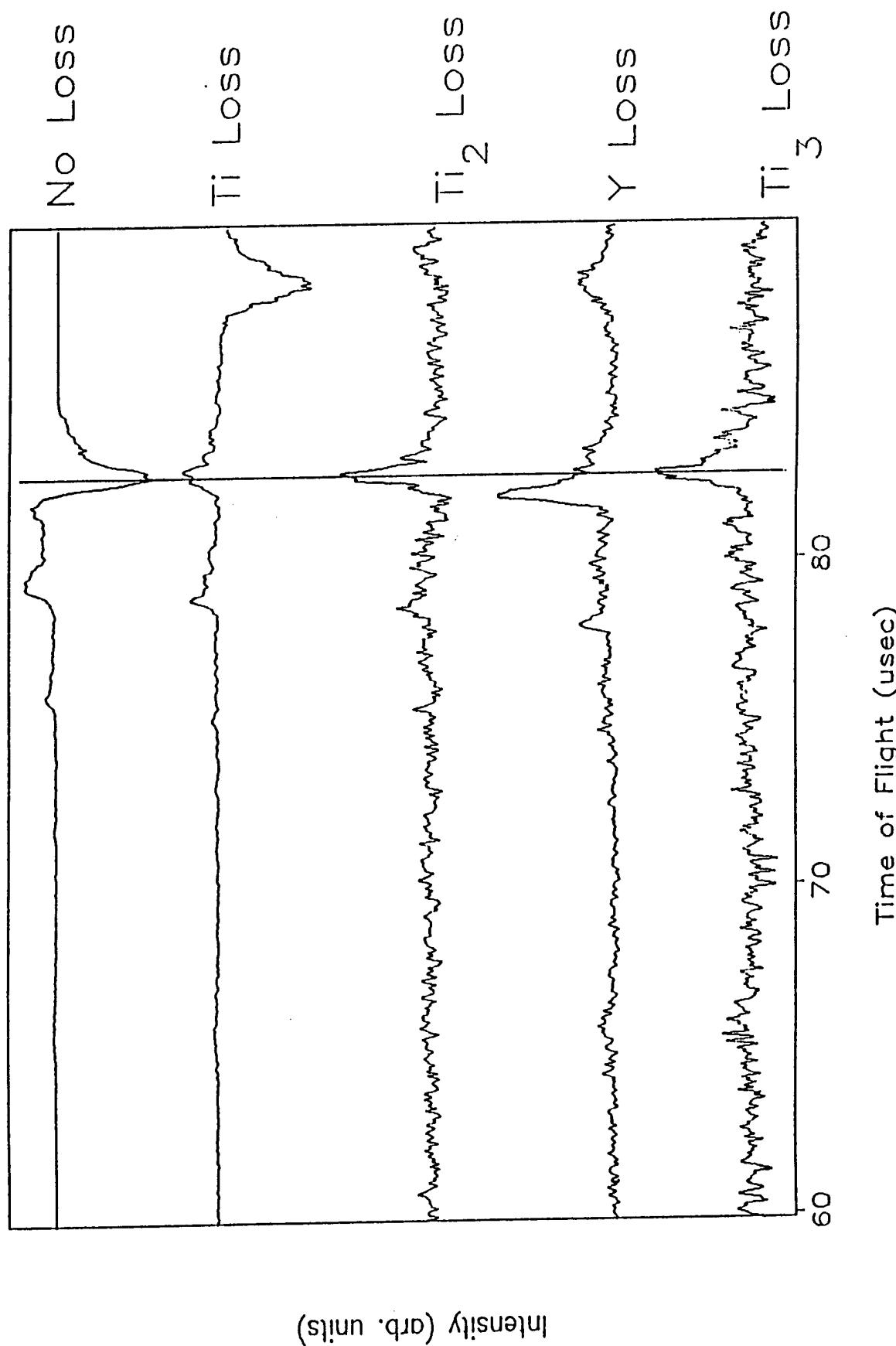
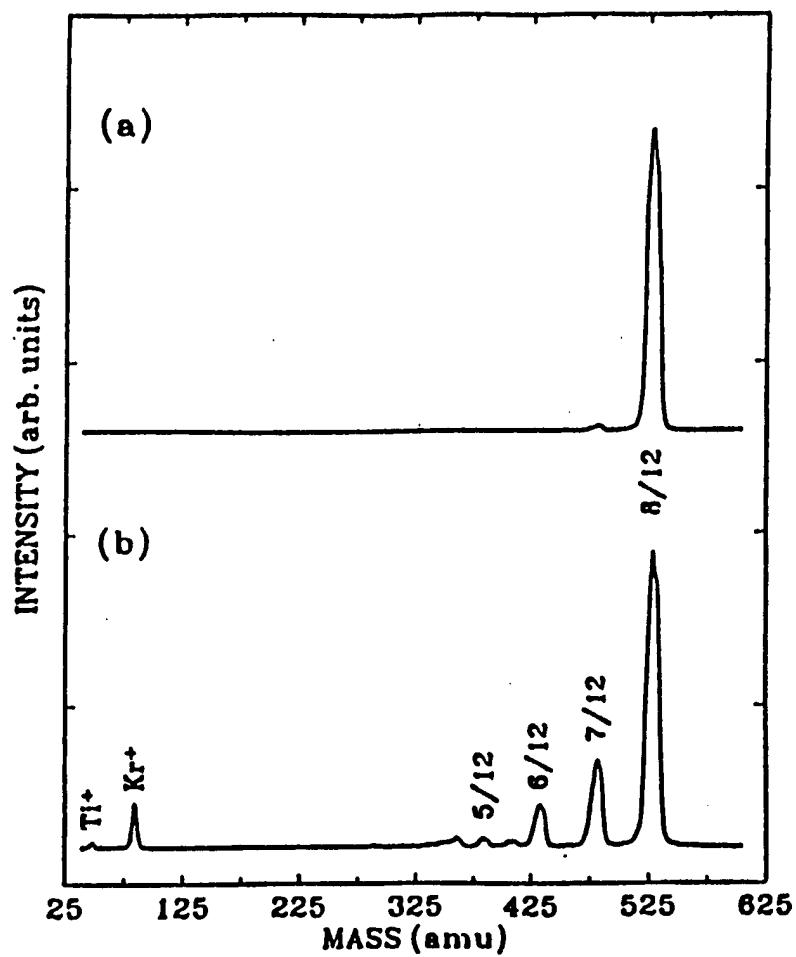


Figure 7. Schematic of the Photoionization-Photodissociation Time-of-Flight Apparatus

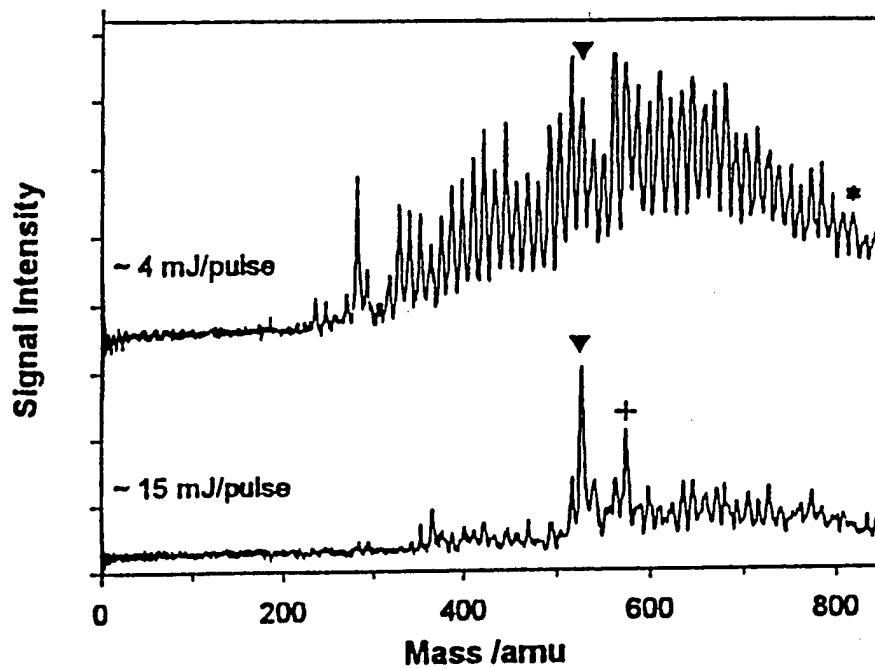
532 nm



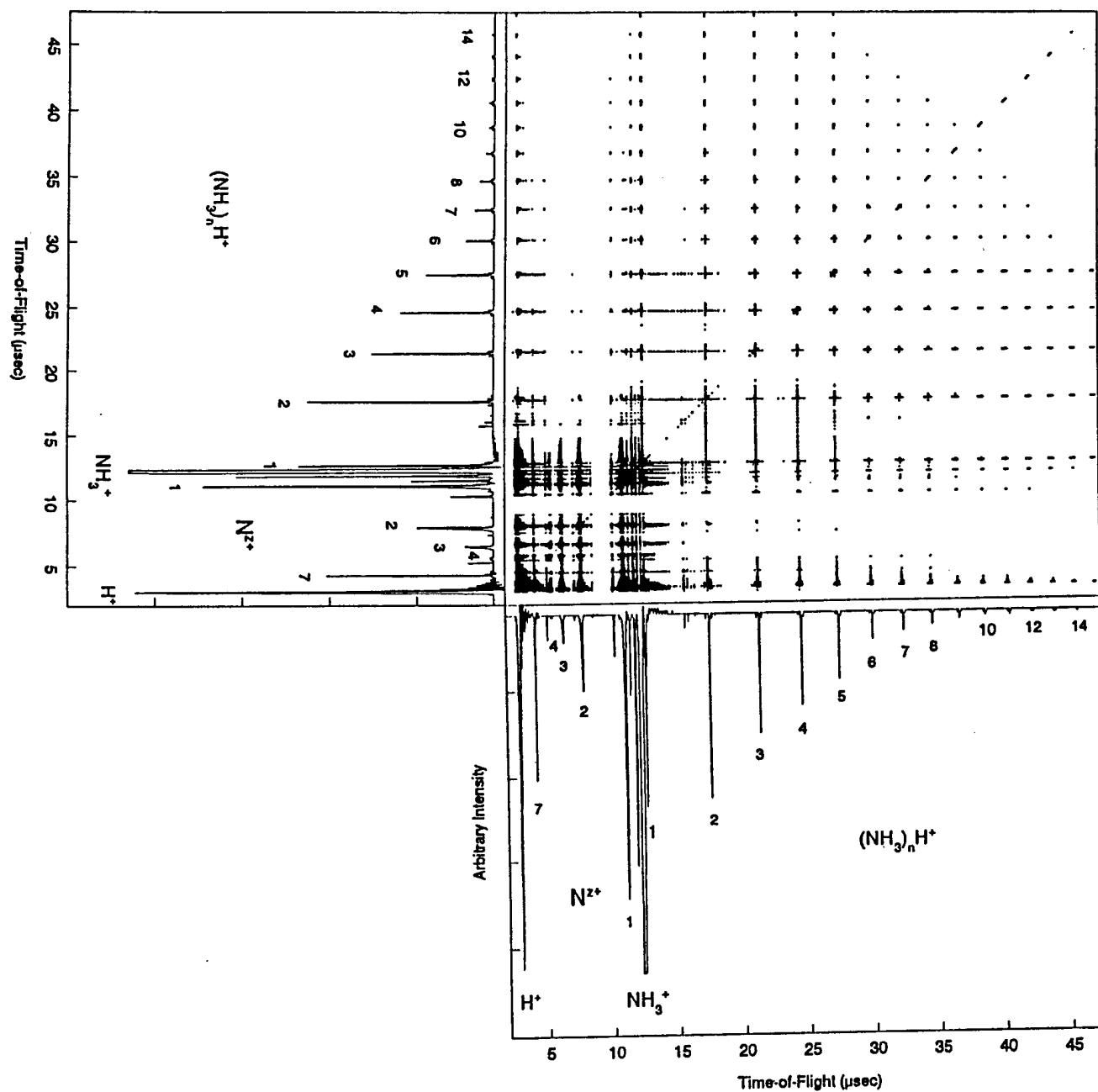
**Figure 8.** Photodissociation scan obtained for  $\text{Ti}_7\text{YC}_{12}$ . The solid line is presented to show the alignment of the various fragment peaks with the original parent depletion. Note that for the trace labeled Y loss, no fragment aligns, therefore Y loss is not observed as a fragmentation channel of  $\text{Ti}_7\text{YC}_{12}$ .



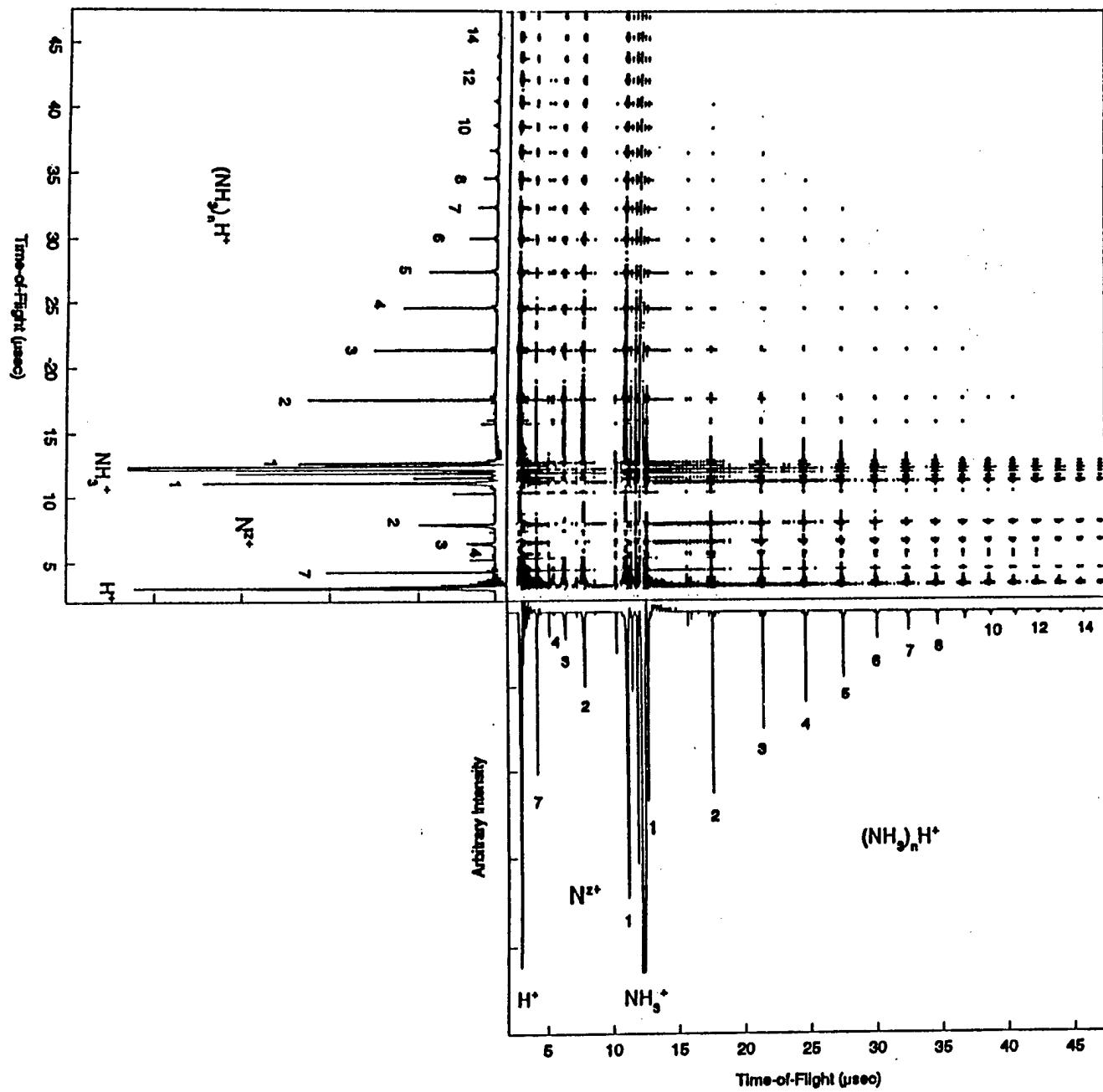
**Figure 9.** CID spectra of  $\text{Ti}_8\text{C}_{12}^+$  at a krypton pressure of  $P_{\text{Kr}}$ : (a) 0.09 mTorr, and (b) 0.7 mTorr, both at a collision energy of 100 eV.



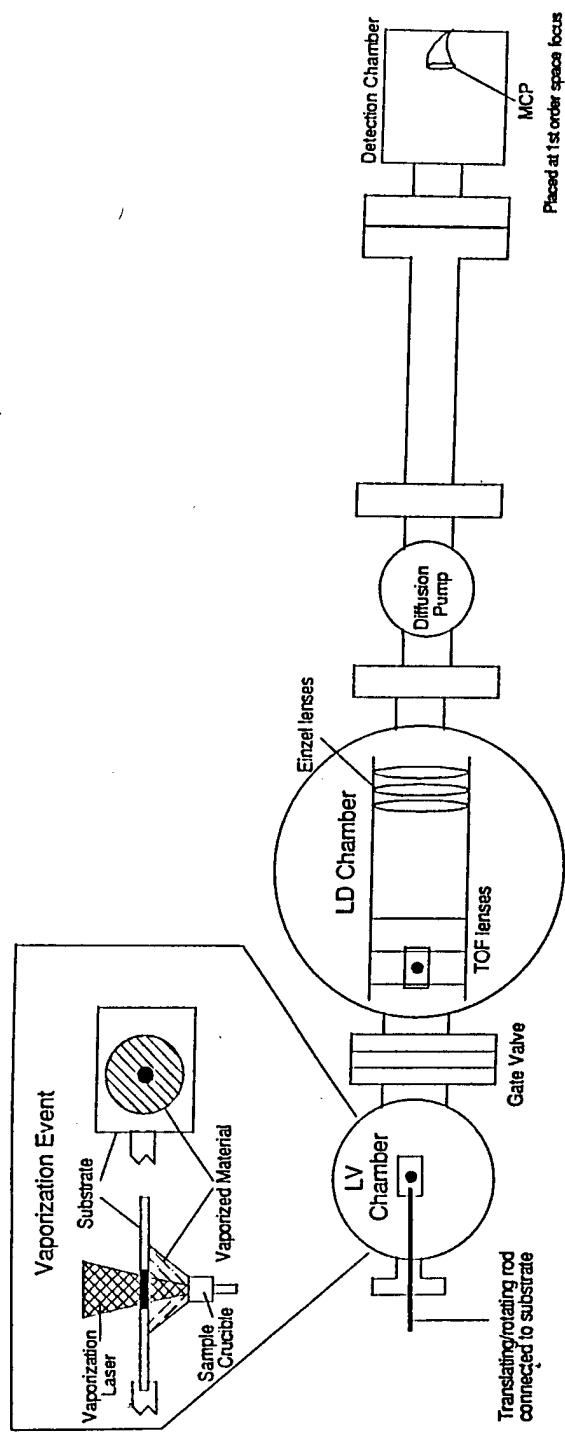
**Figure 10.** Photoionization mass spectra of neutral titanium-carbon clusters produced with two different vaporization laser powers at a constant photoionization condition. Both spectra are plotted in the same scale. The arrows ( $\downarrow$ ) mark the peaks of the  $Ti_8C_{12}$  cluster. The asterisk (\*) shows the position where the  $Ti_{14}C_{13}$  cluster is to appear if it exists. The intense peak marked by the plus (+) is located to the right of the  $Ti_8C_{12}$  peak shifted by 48 amu and hasn't been identified as yet; it is not always present in the mass distribution. The ionization photon energy and laser fluence were 5.17 eV (240 nm) and  $200 \mu J \text{ cm}^{-2}$ , respectively. The data were smoothed without losing primary features.



**Figure 11.** Covariance map of ammonia clusters. The abscissa and ordinate display a TOF spectrum of ammonia clusters averaged over 10,000 single-shot spectra. The center of the figure displays the calculated covariance map as described in the text. Symmetry is clearly visible on the x-y axis starting at the lower left corner. Coupled species are identified by their covariance.



**Figure 12.** Anticovariance map of ammonia clusters. The abscissa and ordinate display the TOF spectrum averaged over 10,000 single shots. Proof of the competitive reaction is seen in the CEP cluster covariance field which was absent in the similar domain of Figure 11.



**Figure 13.** Laser vaporization/laser desorption time-of-flight mass spectrometer.

**Table 1.** Summary of the various photofragments reported for the photodissociation of single metal containing Met-Cars. Each successive neutral loss is indicated under the column which indicates the remaining observable ion fragment. An X indicates that the parent for this step is unknown.

	7/12	7/10	6/12	6/10	6/9	5/12	5/8	5/7	4/12	4/6	3/12	2/12	3/2	2/2	1/0
Ti <sub>4</sub> C <sub>12</sub>	M		M			M									X
Zr <sub>4</sub> C <sub>12</sub>	M			MC <sub>1</sub>		MC <sub>1</sub>				MC <sub>1</sub>					X
Cr <sub>4</sub> C <sub>12</sub>	M		M			M			M		M	M	X	X	X
Fe <sub>4</sub> C <sub>12</sub>	M		M			M			M		M	M	X	X	X
Mo <sub>4</sub> C <sub>12</sub>		MC <sub>1</sub>			M <sub>2</sub> C <sub>1</sub>			M <sub>2</sub> C <sub>1</sub> MC <sub>2</sub>		M <sub>2</sub> C <sub>1</sub>					X

**Table 2.** Summary of the photofragments observed for singly substituted binary metal Met-Cars.

	Ti <sub>6</sub> MC <sub>12</sub>	Ti <sub>5</sub> MC <sub>12</sub>	Ti <sub>4</sub> MC <sub>12</sub>
Ti <sub>7</sub> YC <sub>12</sub>	Ti	Ti	Ti
Ti <sub>7</sub> ZrC <sub>12</sub>	Ti	Ti	Ti
Ti <sub>7</sub> NbC <sub>12</sub>	Ti	Ti	

**Table 3.** Peak ratios of various Zr<sub>x</sub>C<sub>y</sub> species to Zr<sub>8</sub>C<sub>12</sub>.

Experiment	Zr <sub>6</sub> C <sub>12</sub>	Zr <sub>4</sub> C <sub>y</sub> : Zr <sub>6</sub> C <sub>12</sub>
Molecular beam	10 : 1	3 : 1
DLV gas-phase	10 : 1	1 : 1
LD of a LV sample	2 : 1	.36 : 1